



National Institute of Standards & Technology

Report of Investigation

Reference Material 8506a

Water in Transformer Oil

This Reference Material (RM) is intended for use in developing and validating methods for the determination of water in transformer oil or similar matrices. A unit of RM 8506a consists of five ampoules with each ampoule containing 9.5 mL of petroleum electrical insulating oil.

Reference Concentration Values: Four reference values for water content are provided. Three reference values are based on the coulometric method of ASTM Standard D 1533-99 [1], and one is based on a NIST modification to the volumetric method of ASTM Standard D 1533-96 [2]. A reference value is a noncertified value that is the best estimate of the true value; however, the value, which is based on a single reliable method, does not meet the NIST criteria for certification and is provided with an associated uncertainty that may reflect only the measurement precision and may not include all sources of uncertainty. The first coulometric value is the NIST result corrected for the coulometrically detected material present in the oil that reacts with iodine but is not water (interfering substances). Because the correction is new, two additional uncorrected values determined by the coulometric method in ASTM Standard D 1533-99 are provided: the NIST result, and a consensus result obtained from an interlaboratory study conducted among 14 laboratories from industry. The volumetric reference value, which has not been corrected for interfering substances, is significantly different from the coulometric results. Applying the coulometrically determined correction for interfering substances does not resolve this difference. The basis of the difference between coulometric and volumetric results in this material has **NOT** been fully resolved.

Reference Values for Water Content

NIST coulometric mass concentration of water, ASTM method minus interferences: $12.1 \text{ mg/kg} \pm 1.9 \text{ mg/kg}^a$

(NIST coulometric mass concentration of water, ASTM method: $18.3 \text{ mg/kg} \pm 1.9 \text{ mg/kg}^a$)
(Consensus coulometric mass concentration of water, ASTM method: $21.2 \text{ mg/kg} \pm 1.7 \text{ mg/kg}^b$)

NIST volumetric mass concentration of water, modified ASTM method: $34.5 \text{ mg/kg} \pm 2.2 \text{ mg/kg}^c$

^a The coulometric values are expressed as the mean \pm the expanded uncertainty. The expanded uncertainty in these values is equal to $U = ku_c$, where u_c is the combined standard uncertainty calculated according to the ISO Guide [3] and k in the coverage factor. The value of u_c is intended to represent, at the level of one standard deviation, the combined effect of the uncertainties in the reference value. Uncertainty in the bias of the method is not included. Here u_c is given by the standard uncertainty of the mean of the values. The coverage factor k is the Student's t -value for the 95 % confidence interval with three degrees of freedom.

^b The consensus coulometric result is expressed as the mean \pm the expanded uncertainty. This was calculated as above with the exception that there were 12 degrees of freedom.

^c The volumetric reference value is expressed as the mean \pm the expanded uncertainty. This value was calculated in the same way as the coulometric reference values with the exception that there were three degrees of freedom.

Expiration of Reference Value: The reference value of the water content of RM 8506a is valid, within the measurement uncertainty specified, until **31 December 2010**, provided the RM is handled in accordance with instructions given in this Report of Investigation (see *Instructions for Use*). This reference value is nullified if the RM is damaged, contaminated, or modified.

The support aspects involved in the preparation, analysis, and issuance of this RM were coordinated through the NIST Standard Reference Materials Group by B.S. MacDonald.

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Gaithersburg, MD 20899
Certificate Issue Date: 29 October 2002
See *Certificate Revision History* on Page 3

The coordination of the technical measurements was under the direction of S.A. Margolis and S.A. Wise of the NIST Analytical Chemistry Division.

Preparation of the material and the analytical measurements leading to the reference values were performed by S.A. Margolis of the NIST Analytical Chemistry Division.

Consultation on the statistical design of the experimental work and evaluation of the data were provided by M. Levenson and J. Filliben of the NIST Statistical Engineering Division.

INSTRUCTIONS FOR USE

Handling: This material contains no detectable concentration of polychlorinated biphenyls (PCBs) (ASTM Standard D 4059). It should be used with caution around heat, sparks, pilot lights, static electricity, and open flame. Proper disposal methods should also be used. The ampoules are sealed under dry argon. After opening the ampoules, exercise care to avoid contamination with water (e.g., dry measuring devices and containers must be used). The Material Safety Data Sheet (MSDS) that accompanies this RM provides additional information on the material.

Storage and Stability: Ampoules should be stored in the dark at room temperature. No change in the water content occurred in RM 8506 over seven years stored at ambient (room) temperature.

Use: For the reference value to be valid within the stated uncertainty, samples of the material for analysis should be withdrawn from the ampoules immediately after opening and used without delay. The reference value is not applicable to material left in ampoules that have been stored after opening, even if they are resealed.

PREPARATION AND ANALYSIS

Preparation: The oil used to prepare RM 8506a was from the same lot as that used previously for RM 8506. It was obtained from Tilley Chemical Co., Baltimore, MD as UNIVOLT N61 oil manufactured by Exxon Corporation, Houston, TX. At NIST, the material was drawn from a barrel into a clean, dry bottle under an argon atmosphere. Aliquots of 9.5 mL were dispensed automatically from the bottle into argon-filled, dry ampoules, which were then sealed. The reference value therefore, reflects the water content after processing at NIST and not the content as received from the manufacturer.

Analytical Methods: Three reference values for the water content of RM 8506a are reported that are based on the coulometric Karl Fischer Method contained in ASTM Standard D 1533-99 [1]. The first value is corrected for substances ($6.2 \text{ mg/kg} \pm 0.9 \text{ mg/kg}$) that react with iodine but are not water. These interfering substances were determined using a method developed at NIST [6]. However, because this is a new method that is not currently employed by industry, we also report two additional uncorrected values that were determined by ASTM Method D 1533-99 [1]. One value is based on measurements made by NIST and the other value is based on the results from an interlaboratory comparison exercise. The ASTM standard method D1533-99 permits the analyst to saturate the vessel solvent with oil before making any measurements and states that the oil layer needs to be reduced periodically to prevent the accumulation of a large upper layer of oil that is not completely suspended in the vessel solvent. Thus, the water being titrated is in suspension rather than in a single-phase solution. The results of the control in the interlaboratory study, SRM 2890 Water Saturated Octanol, indicated that some instruments were not properly calibrated and may have resulted in a slight bias [2]. For those laboratories who use the volumetric Karl Fischer method, NIST has also measured the water in RM 8506a by a volumetric Karl Fischer method that is based on a NIST modification to the volumetric method in ASTM Standard D 1533-96.

The process of titrating water in an oil suspension coulometrically can lead to a large negative bias relative to volumetric determinations. This bias has been characterized in a study by NIST and is described in several publications [2,5]. The results of these studies demonstrate that the accurate measurement of water in oil requires that the oil be completely dissolved in the vessel solvent. When the solution in the titration vessel begins to undergo the transition from a single phase to a suspension, as much as 40 % to 50 % of the water (depending on the composition of the oil) is sequestered in the upper (oil) phase and is no longer accessible to the Karl Fischer reagent [2]. To achieve complete solubilization of an oil-water mixture, adequate amounts of nonpolar solvents such as chloroform or toluene must be present. If they are not present in sufficient amounts, then only a fraction of the water present will be titrated. The problem of incomplete dissolution of the oil sample is not unique to coulometric solvents. The method of volumetric titration also requires the

¹Certain commercial equipment, instruments, or materials are identified in this certificate in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

presence of chloroform or another suitable nonpolar solvent to measure all the water available for titration. Despite a better understanding of related interferences, the difference between volumetric and coulometric measurements in this material has not been fully resolved.

Measurement of Interfering Substances: The NIST water reference value is more accurate than the ASTM-Method value because some oils contain materials that react with iodine and inflate the measurement of water by the Karl Fischer method. A coulometric method was developed for determining the amount of these interfering compounds using a SO₂ free solution that is similar in composition to the Karl Fischer anode reagent [6]. The results of this NIST determination indicate that the content of interferences in this SRM is 6.2 mg/kg \pm 0.9 mg/kg of water equivalents. The combined content of water and interferences is 18.3 mg/kg \pm 1.9 mg/kg water equivalents.

Interlaboratory Comparison Exercise: The coulometric method in ASTM D 1533-99 is the most common method used by industry for water determination in oil [1]; therefore, a consensus value obtained from an interlaboratory comparison exercise using this method was also established. The laboratories participating in this study are listed below. All analyses in the interlaboratory comparison exercise were performed using coulometric Karl Fischer instrumentation and reagents routinely used in the participating laboratories. In this exercise, each of the participating laboratories analyzed single samples from two ampoules of the RM. The consensus value was calculated by an analysis of variance of the results.

Participants in RM 8506a Interlaboratory Comparison Exercise:

S. Ekert, GFS Chemicals, Inc.; Columbus, OH
P. Griffin, Doble Engineering Co.; Watertown, MA
G. Gauger, Cooper Power Systems; Franksville, WI
F. Mees, UMM Electronics Inc.; Indianapolis, IN
M. Smith, Ergon Refining; Vicksburg, MS
R. Stebbins; S.D. Meyers, Inc.; Talmadge, OH
M. Renz, Dixie Services; Galena Park, TX
J. Jalbert, Hydro Quebec; Varennes, Quebec, Canada
B. Noirhomme, Syprotec, Inc.; Point Claire, Quebec, Canada
O. Codina, TXU Business Services; Lancaster, TX
S. Rice, Arizona Public Services; Phoenix, AZ
S. Smith, Rondar, Inc.; Hamilton, Ontario, Canada
M. Hopkin, CSC Scientific; Fairfax, VA
W. Zjrojewski, Mid-Atlantic Regional Materials Testing Laboratory; Norfolk, VA

REFERENCES

- [1] ASTM D 1533-99; *Standard Test Methods for Water in Insulating Liquids (Karl Fischer Method)*; ASTM Annual Book of Standards, Vol. 10.03, West Conshohocken, PA, pp. 1-5 (1999).
- [2] Margolis, S.A.; *Amperometric Measurement of Water in Transformer Oil Using Karl Fischer Reagents*; Anal. Chem. Vol. 67, pp. 4239-4246 (1995).
- [3] *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st Ed., ISO, Geneva, Switzerland, (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office, Washington, DC (1994); available at <http://physics.nist.gov/Pubs/>.
- [4] ASTM D 1533-96, *Standard Test Methods for Water in Insulating Liquids (Karl Fischer Method)*; ASTM Annual, Book of Standards, Vol. 10.03, West Conshohocken, PA, pp. 105-111 (1997).
- [5] Margolis, S.A.; *Source of the Difference between the Measurement of Water in Hydrocarbons as Determined by the Volumetric and Coulometric Karl Fischer Methods*; Anal. Chem. Vol. 71, pp. 1728-1732 (1999).
- [6] Margolis, S.A.; Paulsen, J.; Park E.; *A Novel Method for Determining Substances that Interfere with the Measurement of Water in Oils and Other Chemicals by the Karl Fischer Method*; Anal. Bioanal. Chem. in press.

Certificate Revision History: 29 October 2002 (Updated coulometric reference values; appendix added); 26 January 2001 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Group at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet <http://www.nist.gov/srm>.

APPENDIX

Measurement of the Non-Aqueous Substances That Interfere With the Coulometric Karl Fischer Method by Reacting with Iodine

Compounds that rapidly reduce I_2 , oxidize I^- , or add I_2 to double bonds can compromise the accuracy of the measurement of water by the Karl Fischer reaction. These include such strong reducing agents as stannous salts, thiosulfate, mercaptans, sulfite, and ascorbic acid; oxidizing agents such as chlorine and dichromate; and compounds that add I_2 across an unsaturated bond. These rapid interfering or side reactions can be titrated independently by using a reagent that is similar to the Karl Fischer reagent but lacks the sulfur dioxide and is thus incapable of reacting with water. A number of these types of compounds, which have not been specifically identified, are present in relatively large amounts in some crude oils. This is particularly the case for SRM 2721 Crude Oil (Light-Sour). Summarized below is a method NIST has developed for measuring the interfering substances using a Metrohm 756 coulometer (Brinkmann Instrument Co., Westbury, NY)² with a diaphragm cell in the Karl Fischer mode [6].

A sulfur dioxide-free coulometric reagent solvent was prepared, consisting of 1.4 mol/L imidazole, 0.2 mol/L potassium iodide, 0.5 mol/L trichloroacetic acid, and 40 μ mol/L sodium thiosulfate in methanol. This solution was allowed to stand for at least 12 h. The reagent was then added to both the anode, which contained 30 % volume xylene to increase the solubility of the oils, and the cathode compartments. If over titration was observed, then a small amount of thiosulfate was added to eliminate over titration (approximately 0.4 mL of 0.1 mol/L sodium thiosulfate). The instrument was then calibrated with thiosulfate and the samples were analyzed for the amount of interference present. Two NIST coulometric reference values are reported for water in this report of investigation. The *NIST coulometric mass concentration of water, ASTM method value* represents the total Karl Fischer reacting material and includes the interferences. The *NIST coulometric mass concentration of water, minus interferences value* represents the ASTM method value corrected for the interferences.

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